Rough Translation

DE4406431A1 1995-08-31 **Procedure for the production of porous parts with catalytic function** (en) ▾ **Abstract**
English Abstract:

Described is a method of manufacturing porous, gas-permeable, catalytically active components (10) with internal surfaces (15) for the catalysis of chemical reactions. A carrier (12) is impregnated at the surface or in the main body of the carrier with catalytic material (13, 14), in particular a noble metal or a getter material such as an alkaline-earth oxide. The impregnated carrier (12) is then sintered with a ceramic substrate material, the carrier (12) being removed by evaporation. The catalytic material (13, 14) remains behind on the pore walls. A catalytically active protective layer (10) produced in this way is suitable for use in automobile exhaust-gas sensors.

▾ **Bibliographic Data**

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IPC-ADDL-CL: B01J35/02 20060101A I20051008RMEP (20060101) Advanced20051008 (A I R M EP)
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IPC-ADDL-CL: B01J37/08 20060101A I20051008RMEP (20060101) Advanced20051008 (A I R M EP)

▾ **Patent References Cited-Backward:**

Retrieve Selected

☐	Publication Number	Publication Date	Title	Applicant/Assignee	Cited By
☐	DE4131503A1	1993-04-01	Abgassensor und Verfahren zu dessen Herstellung.	Robert Bosch GmbH	Originates from the search report

	Publication Number	Publication Date	Title	Applicant/Assignee	Cited By
☐	GB1110852A	1968-04-24	Porous catalyst body	VARTA AKTIENGESELLSCHAFT	Originates from the search report

▾Patent References Cited-Forward:

Retrieve Selected

	Publication Number	Publication Date	Title	Applicant/Assignee
☐	DE19834136C1	2000-03-16	Abgasleitung für eine Brennkraftmaschine	DaimlerChrysler AG, 70567 Stuttgart, DE
☐	WO2004047958A2	2004-06-10	VERFAHREN ZUR BESCHICHTUNG EINES KATALYSATORTRÄGERS ENTHALTEND ZWEI UNTERSCHIEDLICHE TEILSTRUKTUREN MIT EINER KATALYTISCH AKTIVEN BESCHICHTUNG UND DADURCH ERHALTENER KATALYSATOR	UMICORE AG & CO. KG
☐	WO2004047958A3	2004-08-26	KATALYSATOR UND VERFAHREN ZUR BESCHICHTUNG EINES KATALYSATORTRÄGERS ENTHALTEND ZWEI UNTERSCHIEDLICHE TEILSTRUKTUREN MIT EINER KATALYTISCH AKTIVEN BESCHICHTUNG	UMICORE AG & CO. KG

▾ Description

English Description:

State of the art

The invention concerns a procedure for the production more porously, more gaspermeabler, catalytically effective parts in accordance with the kind of the principal

claim.

Of the DE-OS 41 31 503 it is well-known, porous, gaspermeable, ceramic parts, to make for example thin layers with catalytic materials for gas sensors. Porous parts are among other things filters, filters, frits, diaphragms, sponges and capillaries or channels exhibiting bodies. As catalytically active materials precious metals and/or precious metal alloys are mentioned. The use of oxides beside metals in only one ceramic(s) part or also in together-bordering spatially ranges from ceramic(s) parts with in each case a catalytic means are descriptive.

During sintering of mixtures of catalytically active materials with ceramic(s) powders the catalytic means are full-enclosed mostly by ceramic(s), whereby a high materials consumption becomes necessary for the acquisition of sufficient catalytic activity. For bringing catalytic materials into porous ceramic parts by impregnation with a salt solution ceramic(s) with means, which coin/shape the cavity form and which attitude to porosity permit, is sintered, impregnated and again heated up. An even distribution of the catalytic means after thermal distance of the form-forming means on the internal surface of the ceramic, permeablen part is not always reached thereby satisfying. Usable surface on the inside of the ceramic part lies catalytically ineffectively fallow.

Usually Thermalruß, graphite, Theobromin, Indigo, Indanthren, polyethylene epoxy waxes and Picein are used as form-coining/shaping means. Parts with fixed measures and forms, which can be manufactured, the selection (EP-A 0,148,622).

Task of the invention is it, using form-forming means figuration regret, porous, permeable parts on surfaces on the inside with even over this internal surface distributed catalytically active means to coat. Form-coining/shaping means, whose surface catalytic means exhibit and which are suitable for automatable production, are a further the subject of the invention.

The task of the invention is solved by the procedure given in the principal claim. A form screen end a means, which is a thermally decomposable, burn outable and/or evaporatable material, makes possible here, to apply on the internal surfaces of the part catalytic materials. The range of the catalytic means in the part, thus specified, increases its effective surface for the purpose of the catalysis.

Because of the higher catalytically effective surface the materials consumption of the catalytic means and the form-coining/shaping means can be reduced with same catalytic effectiveness. A reduction of the catalytically effective part is possible and the mass decrease of the part extends the mobile employment. By the better uniform distribution of the catalytic material a clear improvement of the life span of the part enters. With large form-coining/shaping means it is possible to cover coherent internal surface ranges of the part with catalytic material. Regarding the production of the part the procedure is needed simplified, as no impregnation is more necessary for bringing in the catalytic means, the one thermal subsequent treatment.

If two or more different catalytic means are used, then it is possible to develop under utilization of the architecture of a form-coining/shaping means with the catalytic means a catalyst at the internal surfaces of the part with that the catalytic means in a firm spatial relationship to each other. In addition different density gradients of mixtures of the catalytic means are adjustable. It is no more problem to manufacture a catalyst on the internal surfaces of the part, composed of several layers.

From the characteristics indicated in the Unteransprüchen further advantages result.

By applying the catalytically effective means on the surface of the form-coining/shaping means connected ranges or samples can be provided with catalytic material on the internal surfaces of the part.

It is to be adapted by different catalytically effective means on the surface of the form-coining/shaping means possible catalytic means different chemical reaction conditions. Around for example CO, HC, to convert NOx and O¥ in automobile exhaust gases into the thermodynamic equilibrium are, preferably RH-catalysts with deep, Pt-catalysts at high temperatures next to each other effectively. By the coating according to invention a separation of catalytic means is possible, which would mix otherwise and by it their effect to lose. An alloy formation of Pt with RH can be avoided in such a way.

In particular if the powder grains exhibit approximately spherical shape, a particularly favorable relationship of surface volumes becomes usable with firm pore radius for the catalysis. Furthermore the permeability of the part with well-known dimensions can be stopped purposefully by the choice of the dimensions of form-coining/shaping means and with catalytic means provided form-coining/shaping means.

With procedure according to invention is possible it to bind the catalytic means in a simple manner to the form-coining/shaping means.

An additive from Theobromin to thick-film pastes and/or ceramic molding materials of the basic substance of the part, during sintering sublimates and defined cavities leaves is suitable excellently for the automated screen printing technology.Design

The figure shows a cut by a porous part with catalytically effective coatings on the pore surfaces.

Description of the remark examples

Fig. 1 shows schematically a porous part **10**, which is manufactured in the procedure according to invention. The channel **16** grew together from closed-up pores **12**, whose internal surfaces exhibit **15** catalytic means **13** and/or **14**. Furthermore is insulating, for example spherical, catalytically ineffective pore **17** in the part **10** represented. The porous part of **10** is from zirconium dioxide ceramic(s), the catalytic means **13** is a getter or a getter, preferably from oxides, preferably from alkaline earth metal oxides, and the catalytic means **14** is a precious metal, an in particular platinum or a rhodium. A gas **11**,

for example the exhaust gas of a thermal engine, flows from the surface of the permeablen part of **10** into the channel **16** to the back of the part of **10** and withdraws there. Isolate lying pores are isolated recognizably.

The form-coining/shaping means will become with chemical Fällprozessen, coated by dead separating on Pulverteilchen, by vaporizing Pulverteilchen, by laser-induced decomposition of gases on Pulverteilchen or in the fluid bed with types of dust on the Pulverteilchen with catalytic means **13, 14** or these catalytic means brought into the volume of the form-coining/shaping means. The subsequent treatment of a catalytic platinum layer for the increase of the adhesive strength on Picein took place favourably in the mitrogen-hydrogen mixture stream with 900 degrees Celsius, for rhodium as catalytic means is 1000 degrees Celsius more favourably. As mitrogen-hydrogen mixture a mixture of 10 parts hydrogen and 90 parts nitrogen was used.

For the production of the part of **10** powders, which form the material of the part of **10**, with powders of form-coining/shaping means, which unites catalytic means **13, 14** to exhibit, are mixed, agitated or sprayed preferably and sintered afterwards. The Sintertemperatur of the mixture lies between 500 and 1600 degrees Celsius for zirconium dioxide powders with Piceinpulver of firm grain size of D = 4 micrometers. The contraction of the part of **10** leads to a diameter of the pores, which is smaller than the original grain diameters of the form-coining/shaping means with catalytic means. As form-coining/shaping means with platinum recompensed Picein, with rhodium recompensed Theobromin or with larger form-coining/shaping grains platinum beside rhodium are preferably used. There is also grains with partial coating one or several catalytic means secondary or one on the other applicable. The different particle size and - form is in **Fig. 1** visibly. It is as a modification also conceivably, getter substances, for example LiAlO¥, to begin in place of catalytically active substances.Example 1

For the production of a porous ceramic(s) part a Thermalrußpulver with a grain size of 1 to 150 micrometers grain diameter with a zirconium dioxide powder, which contains weight percentage Yttriumoxid up to 5, with an organic binder and with a softener under additive of a solvent will grind **10**. After sintering with 1600 degrees Celsius one receives a porous ceramic(s) part. Alternatively Indigo, Picein, polyethylene wax or Theobromin as form-coining/shaping means are used.Example 2

For the production of a porous ceramic(s) part **10** with catalytically effective substances a powder is descriptive used as into example 1, after it was coated preceding with platinum. The form-coining/shaping means is recompensed at its surface by chemical Fällprozesse, in particular reduction of metallic salt solutions, which lead to the separation of catalytically effective platinum or rhodium.Example 3

The grain diameters of the Piceinpulvers, the Theobrominpulvers and the catalytically ineffective form-coining/shaping powder are of various sizes selected for vote to the targeted application.Example 4

A powder substance from Theobrominpulver with platinum layer and zirconium dioxide

powder is over-laminated and sintered by a powder substance from Piceinpulver with rhodium layer and zirconium dioxide powder.Example 5

For the production of a rectangular channel of 100 micrometers channel height 165 micrometers thick and 165 micrometers a broad layer from paste is printed on a ceramic substrate and considered by the more largely selected measures the contraction. The paste was descriptive manufactured as in example 1 and 2, however no zirconium dioxide and Yttriumoxid were used. The received pasty mass is imprinted by means of a usual automated silk-screen printing, for example Tamponprint, on a ceramic substrate. After applying a ceramic resist coating this resist coating in the nitrogen stream is strengthened with 900 degrees Celsius. In a following fuel step at air or in oxidizing atmosphere the form-coining/shaping means are arrears-free burned out. Sintering follows with 1600 degrees Celsius.

For the examples specified above it proved favourably as for the Porengröße at the most the 0.2-fachen value of the layer thickness of the ceramic(s) part which can be manufactured to select itself, which corresponded to a range of application of 2 to 15 micrometers. The layer thickness of the applied catalytically effective material on the Formpräger was particularly favourable, if the diameter of the form-coining/shaping grains constituted the tenfold value of the layer thickness of a schichtförmigen catalytic substance. By the grain size of the form-coining/shaping means before definable by means of seven the porosity of the part of **10** becomes definable regarding partial density, permeability and the diameter of the pores. As form-coining/shaping means for ceramic(s) parts are usable dust, suspensions, pastes, granulates, fixed particles or prefabricated volume parts for ceramic(s) partial production.

Claims

Number of Claims: 12

ENGLISH CLAIMS:

1. Procedures for the production more porously, more gaspermeabler, catalytically effective parts (

10

) marked by internal surfaces (

15

) for the catalysis of chemical reactions of or by gases (

11

) or as getter (

13

), by form-coining/shaping means (

12

) for the internal surface (

15

), which at the manufactured part (

10

) are distant,

dadurch,

that the form-coining/shaping means (

12

) catalytic means (

13

,

14

) exhibit, which remain after the burning out out and/or evaporation of the form-coining/shaping means (

12

) in the pores of the part (

10

).

2. Procedure according to requirement 1, by characterized that form-coining/shaping means on their surface are coated with a catalytically effective means (

13

,

14

), which arrives after the thermal distance of the form-coining/shaping means at surfaces on the inside (

15

) of the finished parts (

10

).

3. Procedure according to requirement 1 or 2, by characterized that the assigned individual form-coining/shaping means exhibits different catalytic means (

13

,

14

) on the surface (

15

).

4. Procedures according to requirement 1 or 2, characterized by the use of a mixture of form-coining/shaping grains (

12

), the different catalyst substances (

13

,

14

), in particular Pt and/or RH exhibit.

5. Procedure according to requirement 1, by characterized that as form-coining/shaping

means a powder with essentially spherical grains is used, whose middle grain diameters than the 0,2-fache smallest measure of a schichtförmigen part (

10

) is smaller.

6. Procedure according to requirement 1 or 2, by characterized that the catalytic means (

13

,

14

) is applied as layer on the form-forming grain, whereby the layer thickness is at the most the 0,1-fache of the grain diameters.

7. Procedure after one of the requirements 1 to 6, by characterized that the form-coining/shaping means is a powder, whose grains are coated by chemical precipitation or dead separation or vaporization from the gaseous phase.

8. Procedure according to requirement 7, by characterized that the catalytic coating (

13

,

14

) on the form-forming grains of a thermal subsequent treatment (sinters) it is submitted for the increase of the adhesive strength of the coating.

9. Form-coining/shaping means for the procedure according to requirement 1, by characterized that powders from Picein, Thermalruß, Theobromin, Indigo, polyethylene or mixtures of these materials are used.

10. Catalytic means for the procedure according to requirement l, characterized by the use of active metals or alloys, in particular oxides M

I

N

III

O¥ mixed from RH, Pd and Pt, and/or Gettermaterialen from alkaline-earth oxides or, whereby M are, N of metals, in particular LiAlO¥, are.